

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Polymeric Thickening Agents

We, STYRENE CO-POLYMERS LTD., a Company organised under the laws of the United Kingdom, of 1, Roebuck Lane, Sale, Cheshire, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new polymer salts useful as thickening agents. Thickening agents are used for a large number of industrial purposes. For example, they are used in adhesives; in impregnating or coating compositions for textiles and paper; as anti-settling aids in surface coatings; flocculating agents for sewage wastes; and as flotation agents for ore and coal separation.

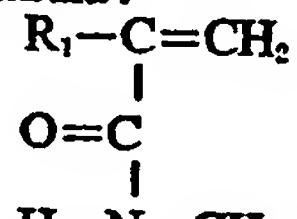
15 A number of thickening agents have been suggested in the past, but these have possessed certain disadvantages. In general, these prior thickening agents have been water sensitive and have remained water sensitive after having been applied to their particular purpose. This has led to substantial disadvantages when the thickening agents have been incorporated in products which are required, at least ultimately, to possess resistance to water, e.g. in certain surface coatings and textile treating compositions. Thus, if the thickening agents are incorporated into a paint which is then applied to a surface and set, the thickening agents which remain water sensitive after

the setting of the paint film reduce the overall water resistance of the paint film.

It is an object of the present invention to provide polymeric thickening agents which, may be cured, after application, to a water insoluble state.

Accordingly the present invention provides as a class of novel compounds useful for the foregoing purposes, water soluble salts of a copolymer comprising units of an N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide and an α,β -ethylenically-unsaturated carboxylic acid.

The N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of the ethylenically unsaturated amide is suitably a compound of the following formula:—



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in which R is an alkyl or cycloalkyl radical having up to twelve carbon atoms and R_1 is hydrogen or a cyano or alkyl radical, or a chlorine atom.

The invention is particularly useful when R in the foregoing formula for the amide has at least two carbon atoms. The ethoxy and higher alkoxy derivatives of the alkyl amides form polymers which are water insoluble and hence cannot be used as such for the said thickening purposes whereas the copolymerisation with the acid accord-

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ing to the invention allows the formation of salts of the copolymer which are soluble in an aqueous medium.

The aforesaid α,β -ethylenically-unsaturated carboxylic acid may be an ethylenically unsaturated monocarboxylic acid, such as acrylic or methacrylic acid; an ethylenically unsaturated polycarboxylic acid, such as itaconic, maleic or fumaric acid; or an ethylenically unsaturated polycarboxylic acid derivative having at least one free carboxylic acid group. The acid will normally constitute at least 7.5% by weight of the total copolymer.

To prepare the salts of the invention, the said amide and said acid are copolymerised together, the reaction generally being carried out in aqueous emulsion at a final non-volatile content of 20-50% by weight. The resultant copolymer emulsion, suitably after thinning, is reacted with a basic substance in order to produce the required water-soluble salt. The basic substance may be an alkali such as ammonium, potassium or sodium hydroxide, or it may be an organic base such as diethylamine, morpholine, hydrazine or an amino-alcohol.

In most cases the carrying out of the copolymerisation in aqueous emulsion causes no especial difficulty. Where R is methyl however, i.e. in N-methoxy methyl acrylamides, the amide monomer is soluble in water as well as in the acid monomers. Accordingly the acid should be so chosen that the partition coefficient of the amide is such that the greater part of the amide monomer is contained in the acid monomer phase, thus permitting the copolymerisation to proceed.

The resultant water-soluble salt, solutions of which are sometimes thixotropic, may be used as a thickening agent. If it is cured after it is applied for its particular purpose, it will become water insensitive. If it has been applied as, or in, a coating, it will form a water insensitive film after curing.

Films produced from copolymers of methoxy methyl acrylamides and copolymerisable acids are hard and brittle and are only suitable in limited applications. Films produced from the methoxy methyl acrylamide copolymers can be made of wider application, and also cheaper, by a modification, described below, comprising incorporating in the copolymer in addition to the methoxy methyl acrylamides and the copolymerisable acid at least one further copolymerisable ethylenically unsaturated monomer.

This modification is however also of value when applied to the copolymerisation of the other amides that can be used in this invention, and especially if the copolymer is used to form a film ie it may be desirable

to modify it so as to achieve certain properties in the film, e.g. flexibility, toughness or hardness. It might even be desired to modify the copolymer if it is to be used other than in, or as, a coating. A great advantage of the new thickening agents is that, the monomers may be adjusted to provide such modification of the resultant copolymer.

This modification may be effected by including one or more extra different ethylenically unsaturated monomers in the copolymer over and above the said amide and said acid. Such extra monomers include vinyl hydrocarbons, such as styrene and -vinyl toluene, and esters of ethylenically unsaturated mono- or poly-carboxylic acids, such as methyl methacrylate, ethyl acrylate, di-n-butyl itaconate, di-n-butyl maleate and di-n-actyl maleate. Partial esters of ethylenically unsaturated polycarboxylic acids can also be used to modify the copolymer, and these can, for example, be the same compounds as the aforementioned ethylenically unsaturated polycarboxylic acid derivatives having at least one free carboxylic acid group which may be used as the acid monomer; in this latter case, only two monomers need be used to prepare the water-soluble salts, namely the said amide and the said partial ester of a polycarboxylic acid.

Instead of or in addition to the above extra monomers, there may be included in the copolymer polar monomers such as acrylonitrile, 2-hydroxyethyl methacrylate or 2-hydroxypropyl methacrylate, e.g. that prepared by the reaction of methacrylic acid and propylene oxide. By "polar monomers" is to be understood monomers having a polar characteristic greater than that of styrene, i.e. having a polar characteristic numerically greater than 0.8 in the scale proposed by Alfrey et al, in "Co-polymerisation" (Vol 8 of the Inter-Science series on High Polymers).

The following broad ranges by weight are given by way of example for monomers used to produce suitable copolymers according to the present invention:—

1. 5-35% of the said N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide.

2. 7.5-30% of the said α,β -ethylenically unsaturated carboxylic acid.

3. 35-87.5% of one or more of the aforementioned additional monomers.

Particularly high molecular weight copolymers can be obtained by including in the copolymerisation a poly-functional monomer, i.e. a monomer containing at least two ethylenically unsaturated double bonds, such as divinyl benzene, glycol di-methacrylate or methylene bis-acrylamide, preferably in an amount of up to 5% by weight of the

total copolymer. With the inclusion of such poly-functional monomers, extremely viscous solutions of the copolymers can be obtained, even at concentrations of 1-3 by 5 weight in water.

Especially useful copolymers can be produced from:—

1. 15.35% of the said N-alkoxyalkyl or 10 N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide.

2. 7.5-30% of the said α,β -ethylenically unsaturated carboxylic acid.

3. 20-65% of an alkyl ester of acrylic or methacrylic acid.

15 4. Up to 5% of a poly-functional vinyl monomer.

5. Up to 10% of a mono-vinyl aromatic hydrocarbon.

20 It has also been found that the thickening agents of the present invention are useful as a sizing agent of a temporary or permanent nature for textiles, particularly those of cellulose acetate fibre.

25 The invention is illustrated by the following Examples in which the parts quoted are by weight:—

Example 1

A. Preparation of Monomer Mixture

30 The following were mixed together:—

N-n-butoxymethyl acrylamide 294 gms.
Ethyl acrylate 400 gms.
Methyl methacrylate 356 gms.

This mixture was washed with:

35 a) 1 litre of 5% aqueous sodium hydroxide

b) 1 litre of water

After washing there remained 1000 gms of monomers to which was added:—

40 i) Methacrylic acid 177 gms.
ii) Lauryl mercaptan 6 gms.

This produced a monomer mixture free from inhibitor.

B. Preparation of Catalyst/Emulsifier Solution

45 Fenopon T 77 (see below) 30 gms.
Ammonium persulphate 5 gms
Water 1285 gms.

These were mixed together to form a catalyst/emulsifier solution.

50 (Fenopon T 77 is sodium N-methyl N-oleoyl taurate and is supplied by General Aniline and Film Corporation N.Y.)

55 Into a glass reaction vessel fitted with stirrer, reflux condenser, thermometer thermoregulator and two dropping funnels, were placed 1315 gms. of water. This was heated to 50°C and 50 mls. each of the above monomer mixture and catalyst/emulsifier solution were added. The temperature was then raised to 90°C and the remaining monomers and catalyst/emulsifier solution as added dropwise over 2-2½ hours.

60 After the addition of components A and B had been completed the resultant emulsion was maintained at 90°C for a further 65

1½ hours and then the mixture was blown lightly with nitrogen for 10 minutes, to remove traces of unreacted monomers. The emulsion was then cooled.

The characteristics of the copolymer 70 emulsion were:

Solids content (1 hour at 140°C) 28.2%

Viscosity (Ostwald method) 15 cp.

pH 4.5

Composition:—

N-n-butoxymethyl acrylamide	23.8%	75
Ethyl acrylate	32.3%	
Methyl methacrylate	28.8-9%	
Methacrylic acid	15%	
Lauryl mercaptan	0.5% (on 80	

total monomers)

The emulsion was thinned to various concentrations between 2 and 5% and neutralised by the addition of a base (ammonia) to give clear, water white solutions. The 85 viscosities of the solutions were measured by two methods involving different rates of shear, the Paint Research Station (PRS) bubble tube method and the Hoeppeler viscometer; and the following results obtained:

Concentration 2.0 2.5 3.0 4.0 5.0

Viscosity PRS	1.0	1.7	10.0	35.0	>200.0
method					
(Poise)					

Viscosity	0.12	0.18	1.2	2.8	17.0
Hoeppeler					
(Poise)					

The very large discrepancies in the results from the two methods is an indication of the thixotropic nature of the solutions.

100 *Example 2*

The procedure was exactly as Example 1 except that the monomer mixture was prepared as follows. There were initially mixed together:

N-n-butoxymethyl acrylamide	177 gms.	105
Ethyl acrylate	400 gms.	
Methyl methacrylate	388 gms.	

After washing as in Example 1, 940 gms. remained and

Methacrylic acid	236 gms.	110
was added.		

After this monomer mixture had been emulsified and copolymerisation had been effected, as set forth in Example 1, the characteristics of the finished copolymer emulsion were:—

Solids content (1 hour at 140°C)	29.8%	115
Viscosity	18 cp	
pH	4.0	120

and the composition of the copolymer was:—

N-n-butoxymethyl acrylamide	14.7%	125
Ethyl acrylate	33.1	
Methyl methacrylate	32.2	
Methacrylic acid	20.0	

The copolymer emulsion was thinned to various concentrations between 2 and 5% and neutralized by the addition of ammonia solution, and the viscosities of the resultant 130 solutions were measured by the Paint Re-

search Station bubble tube method.

The following results were obtained:—
 Concentration 2.0 2.5 3.0 4.0 5.0
 Viscosity in 5.0 9.0 >200 gel gel

5 in poises

Example 3

The emulsion prepared according to Example 2 was used to thicken primers based upon thermosetting acrylic copolymer emulsions. It was found to give improvement in water resistance to the resulting stoved films in comparison to thickening agents which do not have the same cross-linking ability.

15 15 A mill base was prepared from the following:—

Red Iron Oxide	90 parts
Barytes	90 "
Talc	45 "
20 Water	119 "
Tri-n-butyl phosphate	0.7 "
Amberlac 165 (Rohm & Haas Co.)	7.5 "

This mixture was ground on a pebble mill for 16 hours to give a Hegmann fineness >7.

The mill base was halved and each portion was mixed with the following:—

Primal AC 200* (Rohm & Haas Co.) 185
 30 parts

Ethylene glycol mono-n-butyl ether (60% in water) 19.3 parts

*"Primal" is a Trade Mark

The two separate portions were then 35 thickened with the following mixtures, the first containing a good quality thickener as hitherto in general use and the second containing a thickener according to the invention:—

40 1. Acrysol ASE 60* (Rohm and Haas) 2.0 parts

Water — 24.5 "
 Neutralised with dimethylaminoethanol 3.3 "

45 * "Acrysol" is a Trade Mark
 2. Copolymer emulsion from Example 2.

Water 24.5 "
 Neutralised with dimethylaminoethanol 3.3 "

50 The primers were sprayed on to de-greased mild steel panels, stoved for 30 minutes at 175°C and subjected to humidity, salt spray and water soak tests. The 55 primer thickened with the emulsion of Example 2 gave an improvement in these properties over the primer thickened with the prior art thickener.

Example 4.

60 The products according to this invention are ideally suited to the thickening of water based gloss enamels and clear lacquers, especially those based upon emulsion systems.

65 65 A mill base was prepared from:—

Rutile titanium dioxide	800 gms.
Water	300 gms.
Amberlac 165 (Rohm & Haas)	56 gms.
Isophorone	4 gms.

This was ground on a pebble mill for 70 24 hours to give a Hegmann reading of >7.

A thermosetting acrylic emulsion was thickened using the copolymer emulsion product of Example 2 in the following proportions

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Thermosetting acrylic emulsion (50% N.V.C. i.e. non-volatile content)	2,000 gms.
Product of Example 2 (29.8% N.V.C.)	20 gms. 80

After mixing thoroughly the emulsion was neutralised with 5 mls. of .880 ammonia solution and then the mill base was added to give an enamel with a viscosity of 40 seconds F.C. No. 4 at 20°C. The enamel 85 showed no heavy pigment settlement after standing for 1 month. The stoved film on steel, aluminium and asbestos showed good gloss, excellent hardness and water resistance properties.

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Example 5

The products of this invention may be used as thickening agents for air drying emulsion paints. They are particularly useful for the preparation of finishes to 95 which a pattern is applied by brush or trowel, but may be used also for simple brushing paints in conjunction with cellulose type thickeners.

A paint was prepared as follows:—	100
Rutile titanium dioxide	100 parts
Calcium carbonate	10 "
2% NH ₃ -neutralised emulsion product of Example 2	25 "
2% solution of methyl cellulose	25 "
Water	90 "

The mixture was ground on a single roller mill and added to Polyvinyl acetate copolymer emulsion

50% N.V.C. 140 parts 110

The paint showed very little tendency to settle, had good drying properties and water resistance after ageing for 24 hours and was better than a similar paint using methyl cellulose as the sole thickening agent.

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Example 6

The products according to the invention may be used to thicken emulsions used for coating textiles. The following example is 120 illustrative.

A thickener solution was prepared by taking 30 parts of the copolymer emulsion of Example 2, adding 50 parts of water and neutralising with 2 parts of 0.880 ammonia.

125 A thermosetting acrylic aqueous emulsion was prepared containing 40% by weight of a copolymer of 22.3% by weight of styrene, 58% by weight of n-butyl acrylate and 19.7% by weight of N-cyclohexyloxy-

130

methyl acrylamide.

A mixture was then prepared of the following:—

5 45 parts thermosetting acrylic emulsion
 5 45 parts thickener solution
 10 10 parts 10% solution of ammonium chloride.

The same mixture was prepared using a 4% methyl cellulose solution (2% solution 10 has viscosity of 2500 cp.) in place of the thickener solution prepared above.

The thickened emulsions were applied by doctor blades to patterns of Green Cotton Percal. Four coats were applied with intermediate drying. The patterns were embossed at 175°C with 35 lbs. weight on each arm of the embossing roller. The patterns were then cured for 5 minutes at 150°C. The mechanical effects produced 15 from the emulsion thickened with the emulsion of Example 2 were more resistant to washing than were those using methyl cellulose. The S.D.C. (Society of Dyers and Colourists) No. 1 wash was the test 20 method used.

Example 7

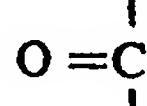
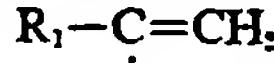
The thickened emulsions prepared according to Example 6 were applied by spreading with a doctor blade on to Green 30 Cotton Percal. The cotton was then combined with polyurethane foam 1/16" thick on a Palme drying cylinder, dried and baked 3 minutes at 150°C.

The bonded systems were then subjected 35 to the S.D.C. No. 1 wash and also charge system dry cleaning. The systems bonded with the emulsion thickened with the product of Example 2 showed good adhesion after both tests. The system using methyl 40 cellulose as the thickening agent showed fair results after the washing tests but failed the dry cleaning tests.

WHAT WE CLAIM IS:—

1. A water-soluble salt of a copolymer 45 comprising units of an N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide and an α,β -ethylenically unsaturated carboxylic acid.

2. A salt according to claim 1 wherein 50 the ethylenically unsaturated amide derivative has the formula



in which R is an alkyl or cycloalkyl radical having up to twelve carbon atoms, and R₁ is hydrogen or a cyano or alkyl radical 60 or a chlorine atom.

3. A salt according to claim 2 wherein R contains at least two carbon atoms.

4. A salt according to any preceding claim wherein the α,β -ethylenically unsaturated carboxylic acid is acrylic, methacry- 65

lic, itaconic, maleic or fumaric acid.

5. A salt according to any preceding claim wherein the portion of the copolymer derived from the carboxylic acid constitutes at least 7.5% by weight of the total copolymer. 70

6. A salt according to any preceding claim wherein the copolymer is derived from the polymerisation of monomers comprising the amide derivative and the carboxylic acid, and in addition, at least one other ethylenically unsaturated monomer. 75

7. A salt according to claim 6, wherein the other ethylenically unsaturated monomer is styrene, vinyl toluene, or an ester of an ethylenically unsaturated mono- or polycarboxylic acid. 80

8. A salt according to claim 6 or 7, wherein copolymer is derived from monomers in the proportions by weight: 85

(1) 5-35% of said N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide;

(2) 7.5-30% of said α,β -ethylenically unsaturated carboxylic acid; and 90

(3) 35-87.5% of one or more other ethylenically unsaturated monomers.

9. A salt according to any of claims 6 to 8 wherein the copolymer is derived from monomers in the proportions by weight: 95

(1) 15-35% of said N-alkoxyalkyl or N-cycloalkoxyalkyl derivative of an ethylenically unsaturated amide;

(2) 7.5-30% of said α,β -ethylenically unsaturated carboxylic acid; 100

(3) 20-65% of an alkyl ester of acrylic or methacrylic acid;

(4) up to 5% of a polyfunctional vinyl monomer; and

(5) up to 10% of a mono-vinyl aromatic 105 hydrocarbon.

10. A salt according to any one of claims 1 to 8 wherein the monomers from which the copolymer is derived include a polar monomer (as hereinbefore defined). 110

11. A salt according to claim 10, wherein the polar monomer is acrylonitrile, 2-hydroxyethyl methacrylate or 2-hydroxypropyl methacrylate.

12. A salt according to any preceding 115 claim wherein the monomers from which the copolymer is derived include a polyfunctional monomer containing at least two ethylenically unsaturated double bonds.

13. A salt according to claim 12 wherein 120 the polyfunctional monomer is di-vinyl benzene, glycol di-methacrylate or methylene bis-acrylamide.

14. A salt according to claim 12 or 13, wherein up to 5% by weight of the total 125 copolymer is derived from the polyfunctional monomer.

15. A water-soluble salt according to claim 1 and substantially as described in Example 1 or 2. 130

16. A surface coating composition containing, as thickening agent, a water-soluble salt according to any preceding claim.
17. A textile treating composition containing, as thickening agent, a water-soluble salt according to any preceding 1-15.
18. A surface coating composition containing a water-soluble salt according to claim 15, and substantially as described in any one of Examples 3-5.
19. A textile treating composition containing a water-soluble salt according to claim 15, and substantially as described in Example 6.
20. Textiles treated with a textile treating composition according to claim 17 or 19.

For the Applicants,
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Reference has been directed in pursuance
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